



This invention relates to the hydrogenation of
1,2,2 trichloropentane, $\text{CF}_3\text{CCl}_2\text{CF}_2$, and its
more particularly directed to 1,2,2 trichloropentane
making this compound and 2 monohydroperfluoropropane,
propane $\text{CF}_3\text{CH}_2\text{CHF}_2$, a new product, and to processes for
objects of the invention include provision of
1,2,2 trichloropentane as a new compound, and
1,2,2 trichloropentane as a new compound, and
methods for making $\text{CF}_3\text{CH}_2\text{CHF}_2$ and $\text{CF}_3\text{CH}=\text{CF}_2$.
In accordance with the invention, it has been
found that, by use of certain catalysts and gas-phase
reaction conditions, hydrogen may be directly substituted
for the chlorine of 1,2,2 trichloropentane,
and that 1,2,2 trichloropentane, 2 monohydro-
perfluoropropane, and 2 monochloropentane, 2
gas-phase
If desired, may be made by direct catalytic gas-phase
pentane, and 2 monochloropentane, 2 monohydro-
hydrogenation of 1,2,2 trichloropentane.
The invention comprises the discovery of the
adaptability of $\text{CF}_3\text{CCl}_2\text{CF}_2$ as an organic starting
material, catalysts and reaction conditions conducive
catalytic reactions, which factors of starting
material, and the discovery of particular catalysts and
afford accomplishment of the invention objectives.

Practice of the invention comprises hydrogenating
1,2,2 trichloropentane by subjecting the same
under certain temperature conditions and while in the
presence of certain catalysts to the action of hydrogen
in quantity and for a time sufficient to effect formation
of a substantial amount of a hydrogenated straight-chain
three carbon atom hydrocarbon consisting of carbon,
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Fluorine, and hydrogen and having respective terminal carbon atoms tri- and trifluorinated and the said trifluorinated carbon atom containing from zero to one hydrogen atom, and recovering such hydrogenated hydrocarbons, which may be $\text{CF}_3\text{CH}_2\text{CHF}_2$ or $\text{CF}_3\text{CH}=\text{CF}_2$ or mixtures thereof, from the resulting reaction products.

The organic starting material, 1,2,2-trichloro-pentafluoropropane, $\text{CF}_3\text{CCl}_2\text{CF}_2$. A known compound, is a colorless liquid boiling at 72° C. Reactions effected during practice of the invention may be represented by -

An important feature of the invention is the nature of the catalytic material employed and the compo-

the catalysts described afford two marked advantages,

namely, facilitate use of moderate reaction temperatures,

and effect high yields of sought-for products, which

yields, within limits may be made selective by alteration

of reaction conditions. With regard to preparation of

the catalyst, a water-soluble palladium salt which is

capable of reduction to elemental palladium by hydrogen

may be employed. Readily available palladium chloride

is preferred. Any of the commercial carbons may

be treated preliminarily to remove any silica by leaching

with aqueous HF, water washing, and drying. The granular,

activated carbon support may be immersed in an aqueous

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Thus, increased temperature and hydrogen concentration
extant upon temperature and hydrogen concentration.

a desired percentage of reaction is dependent to some
extent upon time necessary to effect
contact or residence time necessary to effect
material.

2.5 to 4 mols of hydrogen per mol of organic starting
such quantity as to provide in the reaction zone about
is not desired, it is preferred to employ hydrogen in
tally ultimate formation of $\text{CF}_3\text{CCl}= \text{CF}_2$ if this product
high reaction temperature and to minimize or substanc-
hydrogen per mol of organic starting material. To avoid
and little within the range of about 1.5 to 4 mols of
starting material ratios may be varied considerably
of reactants are noted above. Hydrogen to organic
 $\text{CF}_3\text{CCl}_2\text{CF}_2$ starting material. Stoichiometric amounts
sufficient to react with a significant amount of the
Hydrogen may be employed in any quantity
substantially in the range of 175-350° C.

about 350° C. Accordingly, preferred temperatures lie
advantages accrue by use of temperatures in excess of
hydrogen concentration and residence time no particular
decomposition. However, with reasonably suitable
400° C. may be employed without affecting too undesirable
hydrogen substitution, and temperatures as high as about
175° C. In general, increase in temperature increases
results, temperatures are preferably not less than about
about 150° C., although for commerciality substantial
even for chlorine are effected at temperatures as low as
slight reaction and substitution of hydro-
recovery system.

exit connected to a more or less conventional product

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In view of the intimate relationship between time and vice versa, it has been demonstrated that hydrogenation reactions start with a definite initial rate. An instanteneous reaction has been carried out at the reaction temperature by decomposing a mixture of hydogen and per cent of hydrogen gas under sufficient pressure. The range of 3-4 mol's of hydrogen per mol of catalyst is possible to carry out the reaction conditions substantially without loss of hydrogen. And under sufficient pressure, the catalyst is substituted substantially in the presence of 3-4 mol's of hydrogen per mol of catalyst.

and possible to carry out
as dependent on
the starting material most ratio, and present
interdependent relation of temperature, hydrogenation
state shortener content time and vice versa. In view

15 Long time to effect
inherent increase of concentration of $\text{CF}_3\text{CH}_2\text{CHF}_2$. Thus, by effect of reaction zone exit products containing a
concentration gradient, the reaction may be carried out so as to
effect formation of $\text{CF}_3\text{CCl}=\text{CF}_2$. Contact
time may lie in the range of 2 to 30 seconds. Dependence of products desirably
relative quantity upon the composition and
temperature, mol ratio of hydrogen to organo starting
material, contact time, and catalyst composition may be
determined by test run.

20 weight-for products $\text{CF}_3\text{CH}_2\text{CHF}_2$ and $\text{CF}_3\text{CCl}=\text{CF}_2$
sought-exitting the reaction zone comprise
solutions of $\text{CF}_3\text{CH}_2\text{CHF}_2$ and any unreacted starting material and
hydrogen. Ext products of the reactor may be passed into
a water scrubber which removes last traces of acid, thru a
NaOH solution which removes into a cold trap cooled
 CaCl_2 dryings tower, and thence into a cold trap cooled

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as to products containing
-lignant amount of $\text{CF}_3\text{CH}_2\text{CF}_2$, and, if
relative quantities upon the composition and
temperature, mol ratio of hydrogen to organite starting
material, contact time, and catalyst composition may be
determined by test run.

5 to 10 seconds. Dependences of 2 to 20 seconds,
relative quantities of products desired, with regard to
temperature, mol ratio of hydrogen to organite starting
material, contact time, and catalyst composition may be
determined by test run.

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sought-for products $\text{CF}_3\text{CH}_2\text{CHF}_2$ and $\text{CF}_3\text{CCl}=\text{CF}_2$
hydrogen, HCl , and any unreacted starting material and
water scrubber which removes last traces of the HCl , thru a
 NaOH solution which removes last traces of acid, thru a
 CaCl_2 drying tower, and thence into a cold trap cooled

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by a dry ice-acetone mixture. Any unreacted hydrogen passes thru the cold trap unabsorbed. The varfous constituents of the cold trap condensate may be recovered and isolated by fractional distillation. Any unreacted starting material which might collect in the water scrubber may be recovered by conventional methods. The following illustrates practice of the invention. Percentages are by weight unless otherwise indicated.

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Example 1 - A catalyst consisting of 3% by weight metallic palladium supported on 8-10 mesh Columbta Carbon grade 66 was prepared substantially as follows:

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The reactor was provided at one end with suitable inlets for hydrogen and organic starting material, and the other end with a pipe connection to a products recovery unit. During about 6.5 hours a vesporous mixture of hydrogen were passed at about constant rate into the reactor. Moleular ratio of hydrogen to organic material about 347 g. (1.46 mols) of $\text{CF}_3\text{CCl}_2\text{CCl}_2$ and 4.9 mols

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was about 2.1:1. Exit products of the reactor were handled
reactor. Molecular ratio of hydrogen to organic material
of hydrogen were passed at about constant rate into the
of about 374 g. (1.54 mols) of $\text{Cr}_3\text{C}\text{Cl}_2\text{CCl}_2$ and 3.3 mols
Example 1. During about 4.5 hours a vaporous mixture
temperature and residence time were the same as in
Example 2 - Apparatus, catalyst, reaction

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C-F bonds with no unsaturation.

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134. Infrared analysis showed presence of hydrogen and
the 14° C. $\text{Cr}_3\text{CH}_2\text{CF}_2$ fraction indicated a value of about
61-62%. Molecular weight determination with regard to
material was about 93%. Hydrogen utilization was about
products was about 86%, and overall recovery of organic
Overall conversion of starting material to reaction

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propene, and about 6-7% of unreacted starting material.
pane, $\text{Cr}_3\text{CH}_2\text{CF}_2$; approximately 10% to monochloropropane-
 $\text{Cr}_3\text{CH}=\text{CF}_2$; about 60% to 1,2,2 trihydroperfluoropropene,
starting material converted to pentafluoropropene,

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quantities represented about 15-16% of the red organic
0.037 mol of $\text{Cr}_3\text{CH}=\text{CF}_2$ and $\text{Cr}_3\text{CH}_2\text{CF}_2$. These recovered
comprised about 0.146 mol of $\text{Cr}_3\text{CCl}=\text{CF}_2$ plus about
loss was about 9 g. The minus 22°-plus 13° C. fraction
mol) of unreacted $\text{Cr}_3\text{CCl}_2\text{CCl}_2$ starting material. Sample

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and identified as $\text{Cr}_3\text{CH}_2\text{CF}_2$; and about 22 g. (0.093
108 g. (0.805 mol) of material boiling at about 14° C.
the range of about minus 25° C. to plus 13° C; about
22° C; about 22 g. (0.183 mol) of material boiling in
29 g. (0.216 mol) of $\text{Cr}_3\text{CH}=\text{CF}_2$ boiling at about minus
to fractional distillation. There were recovered about
condensate, recovered in the cold trap, were subjected
cold trap being unutilized hydrogen. About 190 g. of
by a dry ice-acetone mixture, the gaseous exit of the

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About 159 g. of condensate, recovered in the cold trap, products of the reactor were handled as in Example 1. The run temperature was maintained at about 35° C. Extent hydrogen to organic material was about 3.7:1. Hydrogen about constant rate into the reactor. Molecular ratio of $\text{C}_3\text{CCl}_2\text{CF}_2$ and 4.4 mols of hydrogen were passed at hours a vaporous mixture of about 284 g. (1.19 mols) of time were the same as in Example 1. During about 5.5 Example 3 - Apparatus, catalyst and residence

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about 66%.

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forerun, was about 93-94%. Hydrogen utilization wascovery of organic material including the 6 g. (3%) conversion of starting material to reaction products including the forerun, was about 81-82%, and overall re- and about 12% of unreacted starting material. Overall pentafluoropropane, 29-30% to monochloropropylfluoropropane, converted to pentafluoropropene, 22-23% to 1,2,2-trihydro-

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sented about 26-27% of the fed organic starting material mol of $\text{C}_3\text{CH}_2\text{F}_2$. These recovered quantities repre-

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comprised about 0.452 mol of $\text{C}_3\text{CCl}_2\text{CF}_2$ and about 0.113

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was about 10 g. The minus 22° plus 13° C. fraction material. Sample loss including about a 6 g. forerun, 43 g. (0.185 mol) of unreacted $\text{C}_3\text{CCl}_2\text{CF}_2$ starting at about 14° C. and identified as $\text{C}_3\text{CH}_2\text{CH}_2\text{F}_2$; and about plus 13° C; about 31 g. (0.232 mol) of material bottling material bottling in the range of about minus 22° C. to bottling at about minus 22° C; about 91 g. (0.565 mol) of

there were recovered about 54 g. (0.410 mol) of $\text{C}_3\text{CH}_2\text{CF}_2$ as in Example 1. About 259 g. of condensate, recovered in the cold trap, were subjected to fractional distillation.

CF₃CH=CF₂ and CCl₂F=CF₂, which copolymers may be made
CF₃CH=CF₂ is useful in the production of copolymers of
insecticides, commonly used in aerosol compositions.
unites, such as hydrocarbons, plasticizers, polymers, and
with and solubility of many dilutants and active constituents
presence of hydrogen in the molecule increases miscibility
is especially suitable for this purpose because the
functioning similarly to the well known CCl₂F. CF₃CH₂CF₂
CCl₂F₂, CHCl₂F, and CH₃CCl₂F used in aerosol formulations,
adaptable for use as a diluent of propellants such as
liquid having a boiling point of 14° C., is notably
CF₃CH₂CF₂, being a colorless non-flammable
Hydrogen utilization was about 71%.

recovery of organic material were practically 100%.

of starting material to reaction products and overall
1,2,2 trihydroperfluoropropane. Overall conversion
converted to pentafluoropropene, and about 59-60% to
about 40-41% of the fed organic starting material
CF₃CH₂CF₂. Percentagewise, the quantities represented
mol recovery of CF₃CH=CF₂ and 0.715 mol recovery of
CF₃CH₂CF₂. These quantities represent about 0.485
compared about equal weight parts of CF₃CH=CF₂ and
plus 13-14° C. contained no recoverable CCl₂F=CF₂, and
material. The 29 g. reaction, bottling at about minus 22 to
CF₃CH₂CF₂; and no unreacted CCl₂F=CF₂ starting
bottling at about 14-14.5° C. and identified as
about 82 g. (including a 13 g. hold-up) of material
in the range of about minus 22° C. to plus 13-14° C;
at about minus 22° C; about 29 g. of a reaction bottling
recovered about 149 g. of a CF₃CH=CF₂ reaction bottling
were subjected to fractional distillation. There were

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by conventional polymerization processes employing redox catalyst, and which copolymers are useful in the preparation of molded products and coating applications for corrosion protection, e.g., wire coating.

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products.

$\text{CF}_3\text{CH}_2\text{F}_2$, and recovering $\text{CF}_3\text{CH}_2\text{F}_2$ from such reaction products containing a dominant weight proportion of time sufficiently long, to effect formation of reaction substantially in the range of $250-350^\circ\text{C}$. and for residence and under sufficiently high temperature conditions substantially under $3-4$ mols of hydrogen per mol of $\text{CF}_3\text{CCl}_2\text{F}_2$, the range of hydrogen concentration conditions substantially in catalyst, to the action of hydrogen, under sufficiently high hydrogen concentration conditions substantially in the presence of palladium-activated carbon while in the presence of palladium-activated carbon pentafluoropropene which comprises subjecting the same, 2. The processes of hydrogenating 1,2,2-trichloro-

resulting reaction products.

and recovering such hydrogenated hydrocarbon from the carbon atom containing from zero to one hydrogen atom, tri- and difluorinated and the said difluorinated hydrogen and having respective terminal carbon atoms atom hydrogen comprising of carbon, fluorine and amount of a hydrogenated straight-chain three carbon a time sufficient to effect formation of a substantial catalyst, to the action of hydrogen in quantity and for and while in the presence of palladium-activated carbon at temperatures substantially in the range of $175-350^\circ\text{C}$. pentafluoropropene which comprises subjecting the same, 1. The processes of hydrogenating 1,2,2-trichloro-

as follows:

exclusive property or privilege is claimed are defined The embodiments of the invention in which an

